THE MISSING e^4 PERTURBATION THEORY TERMS FOR AN ELECTRON-ION SYSTEM

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1. INTRODUCTION AND SUMMARY

There is a strong interest in the exact computation of as much as is possible about the equation of state of matter under extreme conditions. One such approach is the use of finite-temperature, many-body Matsubara perturbation theory [1]. Gell-Mann and Brueckner [2] have computed the expansion in powers of e, the charge on the electron, through the order e^3 . This achievement was very significant in as much as the expansion is nominally in powers of e^2 . They showed that although the terms corresponding to each diagram in the so called family of "ring diagrams" were divergent, when one sums all of them up the result is finite, but the leading order behavior is not the nominal e^4 behavior which one had expected, but instead the leading order is e^3 ! Their result is for the high-density case of a zero temperature electron gas with a neutralizing positively charged background. Since they were working at zero temperature, they used the standard perturbation theory and not that of Matsubara. In two previous papers [3-4] we have extended these results to all densities and temperatures, and have begun the extension of the expansion to order e^4 . In reference [4] we stated that there were still some terms missing from our results in order e^4 . Specifically these terms are the corrections to the infinite sum of "ring diagrams" which rearrangement of the zero temperature series Gell-Mann and Bruckner found to be necessary to make the perturbation series useful. We compute these missing terms in this paper, but shortness of space precludes the provision of the full details.

In the second section we review some of the details of the perturbation theory, and lay the basis necessary for the computation of the missing terms. In the third section we compute the missing terms for materials which are pure elements. In the fourth section we solve the fugacity equations which allow us to replace the theoretical variables, the electron and the ion fugacities, with directly observable quantities such

as the density and the temperature. We also give plots which show the relative importance of various terms in the perturbation exapansion. Finally in the fifth section we consider the low density ionization limit, in the high temperature region. We compare this limit with the Saha equation, and find that the latter needs some modification.

2. PERTURBATION THEORY

The system that we will treat here is defined by the Hamiltonian,

$$H = \sum_{i=1}^{ZN} \frac{p_i^2}{2m} + \sum_{j=1}^{N} \frac{P_j^2}{2M} + \sum_{i < j}^{ZN} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} - \sum_{i=1}^{ZN} \sum_{j=1}^{N} \frac{Ze^2}{|\vec{r}_i - \vec{R}_j|} + \sum_{i < j}^{N} \frac{Z^2e^2}{|\vec{R}_i - \vec{R}_j|}, \quad (2.1)$$

where \vec{r} , \vec{p} are the position and momentum for the electrons and \vec{R} , \vec{P} are for the ions of charge Z. To treat our problem we employ finite-temperature perturbation theory (Matsubara) [1]. We will treat the electrons as Fermions and the ions as Maxwell-Boltzmann particles.

To begin, we note that $p\Omega$ is a thermodynamic potential [5], where p is the pressure and Ω is the volume. It is equal to $-kT\log \mathcal{Q}$ where k is Boltzmann's constant, T is the absolute temperature, and \mathcal{Q} is the partition function from the grand canonical ensemble. In terms of other thermodynamic quantities $p\Omega = TS + \mu N - U$, where S is the entropy, μ is the Gibbs free energy, or thermodynamic potential, per particle, N is the number of particles, and U is the internal energy. The perturbation series for the pressure is related to that for the energy by the observation that,

$$\frac{\partial(-kT\log\mathcal{Q})}{\partial e^2} = e^{-2}\langle V\rangle,\tag{2.2}$$

where V is the interaction potential, i.e., everything proportional to e^2 in (2.1). Thus,

$$p\Omega = \int_0^{e^2} e^{-2} \langle V \rangle de^2 + p_0 \Omega, \qquad (2.3)$$

relates the series for the energy and that for the pressure. Note that, of course, the wave function changes as e increases in the integral.

The perturbation theory starts off easily enough. The first term (order e^2) is represented by the diagrams in Fig. 1. The direct term D1 vanishes by electrical neutrality. Using the rules of Matsubara theory, we get,

$$p_{E1} = -\frac{4\pi e^2}{(2\pi)^6} \int \frac{d\vec{k}_1 d\vec{k}_2}{(\vec{k}_1 - \vec{k}_2)^2} n(\vec{k}_1) n(\vec{k}_2), \tag{2.4}$$

where

$$n(\vec{p}) = \frac{1}{\exp\{\left[\epsilon(\vec{p}) - \mu\right]/(kT)\} + 1} = \frac{1}{2} \left[1 - \tanh\left(\frac{\epsilon(\vec{p}) - \mu}{2kT}\right)\right]. \tag{2.5}$$

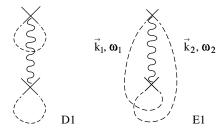


Fig. 1. The diagrams for the first-order interaction in e^2 .

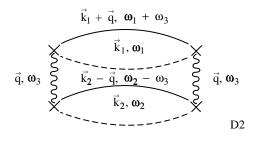
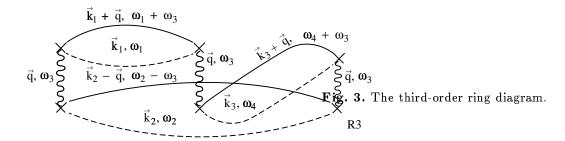


Fig. 2. The second-order direct-interaction diagram.



Next we proceed to examine the nominally second-order in e^2 , direct term, (order e^4 ?!) as represented in Fig. 2. The first thing we notice is that the integral over the momentum labeled \vec{q} in the figure is divergent as $q \to 0$. The solution to this problem was given by Gell-Mann and Brueckner [2]. They summed up all the "ring diagrams." The diagram corresponding to the next "ring term" is given in Fig. 3. This sum is expressed as,

$$-\frac{kT}{2(2\pi)^3} \sum_{\omega_3} \int d\vec{q} \left\{ \frac{\left[8\pi e^2 \Xi(\vec{q}, \omega_3)\right]^2}{q^2 - 8\pi e^2 \Xi(\vec{q}, \omega_3)} \right\}. \tag{2.6}$$

When we convert (2.6) to the series for the $p\Omega$, by (2.3), we get, interchanging the orders of integration,

$$-\frac{kT}{2(2\pi)^3} \sum_{\omega_3} \int d\vec{q} \left\{ \ln \left[1 - \frac{8\pi e^2}{q^2} \Xi(\vec{q}, \omega_3) \right] + \frac{8\pi e^2}{q^2} \Xi(\vec{q}, \omega_3) \right\}. \tag{2.7}$$

where

$$\Xi(\vec{q}, \omega_3) = \frac{1}{(2\pi)^3} \int \frac{[n(\vec{k}) - n(\vec{k} - \vec{q})] d\vec{k}}{-i\omega_3 + \epsilon(\vec{k}) - \epsilon(\vec{k} - \vec{q})}.$$
 (2.8)

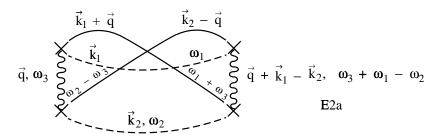
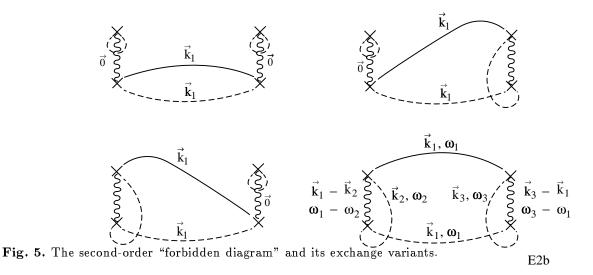


Fig. 4. The second-order exchange-interaction diagram.



To leading order in e^2 , only the $\omega_3 = 0$ term contributes. Following Gell-Mann and Brueckner [2], the result is found to be of the order e^3 and is called the Debye-Hückel term. There are corrections to this term of the order e^4 , but they are the subject of the next section.

In Fig. 4, we show the second order exchange term. It contributes in a straight forward manner an e^4 term. In addition, there are the second order in e^2 "forbidden diagrams" which are shown in Fig 5. They do not occur in zero temperature perturbation theory because the have two parallel lines with the same momentum. However they do occur in finite temperature perturbation theory. Only the one labeled E2b makes a non-zero contribution.

3. THE MISSING TERMS

Our previous report [4] on this general topic was incomplete because of what we called the "missing terms." These terms are the e^4 corrections to the Debye-Hückel

term. Substituting in (2.7) both the ion and the electron contributions, we get

$$-\frac{kT}{2(2\pi)^3} \sum_{\omega_3} \int d\vec{q} \left\{ \ln \left[1 - \frac{8\pi e^2}{q^2} [\Xi(\vec{q}, \omega_3) + Z^2 \Xi_{\rm ion}(\vec{q}, \omega_3)] \right] + \frac{8\pi e^2}{q^2} [\Xi(\vec{q}, \omega_3) + Z^2 \Xi_{\rm ion}(\vec{q}, \omega_3)] \right\} + \frac{kT}{2(2\pi)^3} \int d\vec{q} \left\{ \ln \left[1 - \frac{8\pi e^2}{q^2} [\Xi(\vec{0}, 0) + Z^2 \Xi_{\rm ion}(\vec{0}, 0)] \right] + \frac{8\pi e^2}{q^2} [\Xi(\vec{0}, 0) + Z^2 \Xi_{\rm ion}(\vec{0}, 0)] \right\}$$
(3.1)

for the difference between the whole sum of ring diagrams and the leading order term. If we expand this expression for small e^2 we obtain, for the e^4 term,

$$\frac{kT}{4(2\pi)^3} \sum_{\omega_3} \int d\vec{q} \left\{ \left[\frac{8\pi e^2}{q^2} [\Xi(\vec{q}, \omega_3) + Z^2 \Xi_{\rm ion}(\vec{q}, \omega_3)] \right]^2 - \delta_{0,\omega_3} \left[\frac{8\pi e^2}{q^2} [\Xi(\vec{0}, 0) + Z^2 \Xi_{\rm ion}(\vec{0}, 0)] \right]^2 \right\}, \tag{3.2}$$

which, as we will see, yields a finite coefficient for e^4 . The Kronecker delta is denoted by $\delta_{n,m}$. The next correction is expected to be of the order of e^5 .

In the ion case the density function is of Gaussian form [3] which permits the integration over \vec{k} in (2.8) to be evaluated as,

$$\Xi_{\rm ion}(\vec{q},\omega_3) = -\frac{z_{\rm ion}}{kT} \left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}} \int_0^\infty dt \, \exp\left(-\nu^2 t^2 - \frac{\omega_3}{kT}t\right) \sin(\nu^2 t), \tag{3.3}$$

where

$$\vec{q} = \left(\frac{2MkT}{\hbar^2}\right)^{\frac{1}{2}} \vec{\nu}, \qquad z_{\text{ion}} = \exp[\mu_{\text{ion}}/(kT)]. \tag{3.4}$$

Next we consider the result for the electrons. Here we use a series expansion for Ξ in powers of $z = \exp[\mu/(kT)]$. To this end notice that

$$n(\vec{k}) = \sum_{n=1}^{\infty} (-1)^{n+1} z^n \exp[-n\epsilon(\vec{k})/(kT)].$$
 (3.5)

The result is

$$\Xi(\vec{q},\omega_3) = \frac{2}{kT} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \sum_{n=1}^{\infty} \frac{(-z)^n}{n^{\frac{3}{2}}} \int_0^{\infty} dt \, \exp\left(-\frac{\nu^2 t^2}{n} - \frac{\omega_3}{kT} t \right) \sin(t\nu^2). \quad (3.6)$$

After considerable computation, we obtain terms for the following cases. For the electron-electron, $\omega_3 = 0$ we get

$$\frac{8e^4}{kT} \left(\frac{2\pi mkT}{h^2}\right)^3 \left(\frac{\hbar^2}{2mkT}\right)^{\frac{1}{2}} \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-z)^{n_1+n_2}}{(n_1n_2)^{\frac{1}{2}}} H(n_1, n_2), \tag{3.7}$$

Table I.	Series	coefficients	for the	$\omega_3 \neq 0$	correction
	to	the Debye	Hückel	$_{ m term}$	

n	in fugacity	in de Broglie density		
0	0.0000000000 0000000000 E+000	0.0000000000 0000000000 E+000		
1	0.00000000000000000000000000000000000	$0.00000000000 \ 00000000000 \ \mathrm{E}{+000}$		
2	$4.6513774096\ 5163678750\ \mathrm{E}{-003}$	$4.6513774096\ 5163678750\ \mathrm{E}{-003}$		
3	$-3.4963487161\ 6090598808\ \mathrm{E}{-003}$	$-2.0732820793\ 831582707\ \mathrm{E}{-004}$		
4	$2.6015308683\ 2349543112\ \mathrm{E}{-003}$	$9.8879197604\ 3979831\ \mathrm{E}{-006}$		
5	$-2.0076756122\ 2211161956\ \mathrm{E}{-003}$	$-4.2626300883\ 636177\ \mathrm{E}{-007}$		
6	$1.6028131711\ 2774032555\ \mathrm{E}{-003}$	$1.5323092299\ 68351\ \mathrm{E}{-008}$		
7	$-1.3152892745\ 6794096619\ \mathrm{E}{-003}$	-3.9190088396787E-010		
8	$1.1034163301\ 7761627824\ \mathrm{E}{-003}$	$1.6080369966\ 0\ \mathrm{E}{-}012$		
9	$-9.4235995629\ 5790550502\ \mathrm{E}{-004}$	$5.6380750481 \text{ E}{-013}$		
10	$8.1671770419\ 6771805805\ \mathrm{E}{-004}$	$-4.093577309 \text{ E}{-014}$		
11	$-7.1655028481\ 4367263145\ \mathrm{E}{-004}$	$1.70292681 \text{ E}{-}015$		
12	$6.3521151009\ 9370927217\ \mathrm{E}{-004}$	$-3.453999 \text{ E}{-017}$		
13	-5.6811665775 9281693552 E-004	-1.20181 E-018		

where the de Broglie density is $\zeta = [ZN/(2\Omega)][h^2/(2\pi mkT)]^{3/2}$ and

$$H(n_1, n_2) = -\frac{\pi^{\frac{3}{2}}}{24} \left\{ \sqrt{n_1} + \sqrt{n_2} + 2(n_1 + n_2) \left[\frac{1}{\sqrt{n_1}} + \frac{1}{\sqrt{n_2}} - \left(\frac{1}{n_1} + \frac{1}{n_2} \right)^{1/2} \right] \right\}$$
(3.8)

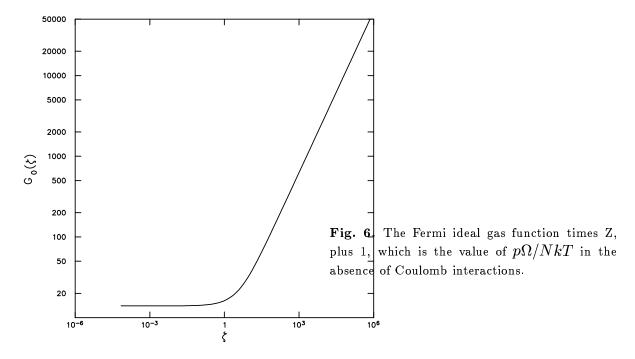
For the electron-electron case with $\omega_3 \neq 0$, we have evaluated the leading order coefficients by means of Romberg integration. The results are listed in Table I.

For the electron-ion case, only the $\omega_3=0$ term contributes significantly in this order as the other terms (when ζ is not large) are of the order of m/M, where m is the electron mass and M is the ion mass. The result is,

$$-\frac{4Z^{2}e^{4}z_{\text{ion}}}{\sqrt{\pi}kT}\left(\frac{2\pi MkT}{h^{2}}\right)^{\frac{5}{2}}\left(\frac{m}{M}\right)\sum_{n=1}^{\infty}\frac{(-z)^{n}}{n^{\frac{1}{2}}}\int_{0}^{\infty}\frac{d\nu}{\nu^{2}}\times\left[{}_{1}F_{1}\left(1;\frac{3}{2};-\frac{m}{4M}\nu^{2}\right){}_{1}F_{1}\left(1;\frac{3}{2};-\frac{n}{4}\nu^{2}\right)-1\right]. \quad (3.9)$$

For the ion-ion terms, the result for the $\omega_3=0$ term is

$$-\frac{\pi Z^4 e^4 z_{\text{ion}}^2}{12kT} \left(\frac{2\pi M k T}{h^2}\right)^{\frac{5}{2}} \left(5 - 2\sqrt{2}\right), \tag{3.10}$$



and the result for $\omega_3 \neq 0$ is just the entry for n=2 in Table I.

4. SOLUTION OF THE FUGACITY EQUATIONS

In this section we need to eliminate the fugacities z and $z_{\rm ion}$ and re-express the thermodynamic quantities in terms of observable variables. From standard quantum statistical mechanics, the required functions may be obtained from the grand partition function \mathcal{Q} by means of

$$\frac{p\Omega}{kT} = \log \mathcal{Q}(\Omega, T, z, z_{\text{ion}}), \tag{4.1}$$

$$ZN = z \frac{\partial}{\partial z} \log \mathcal{Q}(\Omega, T, z, z_{\text{ion}}) \bigg|_{\Omega, T, z_{\text{ion}}},$$
(4.2)

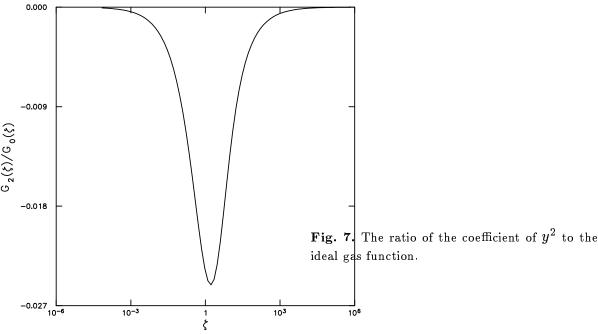
$$N_{\rm ion} = \left. z_{\rm ion} \frac{\partial}{\partial z_{\rm ion}} \log \mathcal{Q}(\Omega, T, z, z_{\rm ion}) \right|_{\Omega, T, z}, \tag{4.3}$$

where $N_{\rm ion} = N$ for system neutrality.

Solving these equations, we get

$$\frac{P\Omega}{NkT} = G_0(\zeta) + G_2(\zeta)y^2 + G_3(\zeta)y^3 + G_4(\zeta)y^4 + o(e^4), \tag{4.4}$$

where $y^2=e^2/(r_bkT)$, and r_b is the radius of a sphere with volume Ω/N . The



coefficients in this expansion are,

$$G_{0}(\zeta) = 1 + Z \frac{2I_{\frac{3}{2}}(z_{0}(\zeta))}{3I_{\frac{1}{2}}(z_{0}(\zeta))}, \tag{4.5}$$

$$G_{2}(\zeta) = -\left(\frac{3Z}{8\pi\zeta}\right)^{\frac{1}{3}} \left(\frac{1}{\sqrt{\pi}}I_{-\frac{1}{2}}(z_{0}(\zeta)) - \frac{1}{\pi\zeta}\hat{X}(z_{0}(\zeta))\right), \tag{4.6}$$

$$G_{3}(\zeta) = -\left(\frac{3}{8\zeta}\right)^{\frac{1}{2}} \left\{\left(Z + \frac{z\frac{d}{dz}I_{-\frac{1}{2}}(z_{0}(\zeta))}{I_{-\frac{1}{2}}(z_{0}(\zeta))}\right) \left[2Z\zeta + \frac{2}{\sqrt{\pi}}I_{-\frac{1}{2}}(z_{0}(\zeta))\right]^{\frac{1}{2}} - \frac{1}{3\zeta}\left[2Z\zeta + \frac{2}{\sqrt{\pi}}I_{-\frac{1}{2}}(z_{0}(\zeta))\right]^{\frac{3}{2}}\right\}, \tag{4.7}$$

$$G_{4}(\zeta) = \frac{1}{4\sqrt[3]{Z}}\left(\frac{3}{\pi\zeta}\right)^{\frac{2}{3}} \left\{\frac{3}{2\pi}I_{-\frac{1}{2}}(z_{0}(\zeta))z\frac{d}{dz}I_{-\frac{1}{2}}(z_{0}(\zeta)) - \frac{1}{2\pi^{\frac{3}{2}}\zeta}\left(I_{-\frac{1}{2}}(z_{0}(\zeta))\right)^{3} + \frac{\sqrt{\pi}}{I_{-\frac{1}{2}}(z_{0}(\zeta))}\left[\frac{1}{2}z\frac{d}{dz}\hat{T}(z_{0}(\zeta)) + z\frac{d}{dz}\hat{\Theta}(z_{0}(\zeta)) + \frac{2}{\sqrt{\pi}}z\frac{d}{dz}\hat{\Psi}(z_{0}(\zeta)) - 4\sqrt{2}z\frac{d}{dz}\hat{\Psi}(z_{0}(\zeta)) - \frac{\pi}{2}Z\frac{\zeta z_{0}(\zeta)}{(1+z_{0}(\zeta))^{2}}\right] - \frac{1}{\zeta}\left[\frac{1}{2}\hat{T}(z_{0}(\zeta)) + \hat{\Theta}(z_{0}(\zeta)) + \frac{2}{\sqrt{\pi}}\hat{\Psi}(z_{0}(\zeta)) - 4\sqrt{2}\hat{\Psi}(z_{0}(\zeta)) - 4Z^{2}\left(\frac{m}{M}\right)^{\frac{1}{2}}\zeta^{2}(0.2776801836)\right]\right\}, \tag{4.8}$$

where

$$I_n(z) = \int_0^\infty \frac{zy^n e^{-y} dy}{1 + ze^{-y}}. (4.9)$$

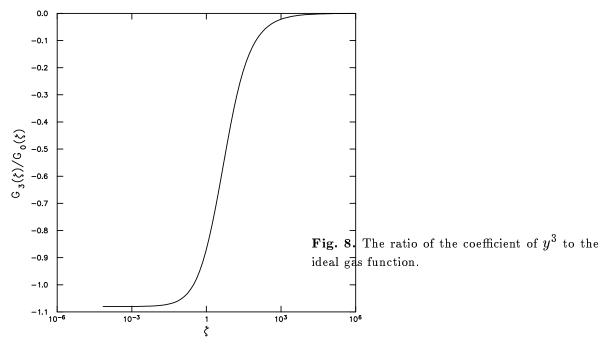
The details of \hat{X} , $\hat{\Theta}$, and \hat{T} are given in reference [4]. The details for $z_0(\zeta)$ are given in reference [3]. The following two equations complete the description of the terms used in the computation of the G's.

$$\hat{W}(z) = \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-z)^{n_1+n_2}}{(n_1 n_2)^{\frac{3}{2}}} \int_0^{\infty} dt_1 \int_0^{\infty} dt_2 \left\{ \exp[2\pi(t_1 + t_2)] - 1 \right\}^{-1}$$

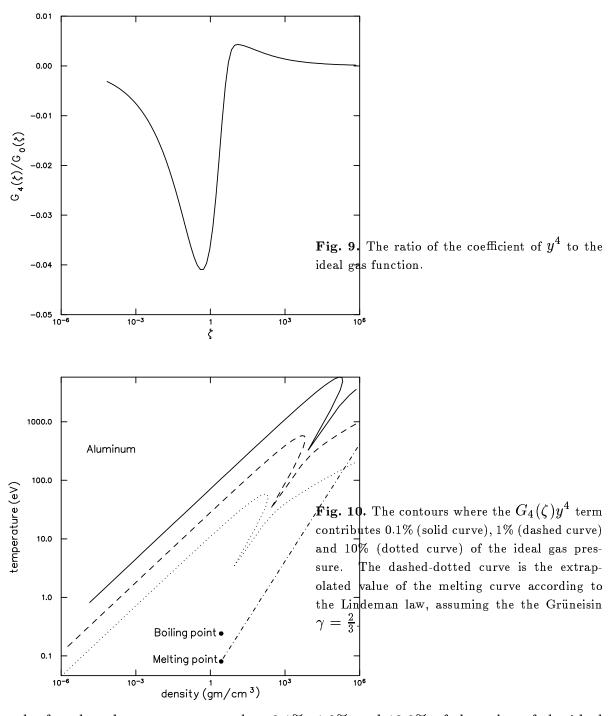
$$\times \left\{ \sqrt{\left[\left(\frac{t_1^2}{n_1} + \frac{t_2^2}{n_2} \right)^2 + (t_1 - t_2)^2 \right]^{\frac{1}{2}} + \frac{t_1^2}{n_1} + \frac{t_2^2}{n_2}} - \sqrt{\left[\left(\frac{t_1^2}{n_1} + \frac{t_2^2}{n_2} \right)^2 + (t_1 + t_2)^2 \right]^{\frac{1}{2}} + \frac{t_1^2}{n_1} + \frac{t_2^2}{n_2}} \right\}. \quad (4.10)$$

$$\hat{\psi}(z) = \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{(-z)^{n_1+n_2}}{(n_1 n_2)^{\frac{1}{2}}} H(n_1, n_2). \quad (4.11)$$

We show in Fig. 6 the ideal Fermi gas function G_0 . In figures 7 - 9, we show the ratios of the G_i 's to the ideal Fermi gas function. These functions are evaluated for the case of Aluminum. It is to be noticed that in the large ζ limit, all these ratios tend to zero, which means that the pressure tends to the ideal gas pressure (for fixed y). In the small ζ limit, the relative size of the coefficients of e^2 and e^4 tends to zero, however that for e^3 remains of order unity.



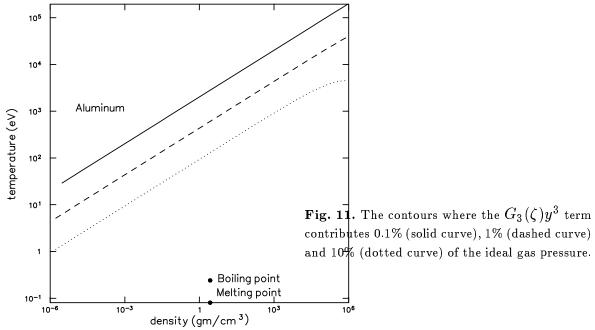
A fuller comparison of the size of the corrections to the ideal gas has been made. In order to gain some indication of the region of validity of the expansion we have computed the values of $y(\zeta)$ for which the third order (most restrictive) and



the fourth order terms are equal to 0.1%, 1.0% and 10.0% of the value of the ideal gas function. These results are plotted in figures 10 and 11, again for the case of Aluminum. The regions above the plotted curves correspond to smaller values of y.

5. LOW DENSITY IONIZATION PROFILE

The results of the previous section allow us to give the leading order terms in the expansion in inverse temperature of the terms of the low density expansion of



the pressure. We complete the results of (4.17) of ref. [4]. Thus we have,

$$\frac{p\Omega}{NkT} = 1 + Z \left\{ 1 - \zeta^{\frac{1}{2}} \left[\frac{\sqrt{2\pi}}{3} (Z+1)^{\frac{3}{2}} \epsilon^3 + \dots \right] + \zeta \left[\frac{1}{2^{\frac{5}{2}}} - \frac{1}{2} \epsilon^2 + \left(\frac{\pi \ln 2}{2\sqrt{2}} + \frac{\pi\sqrt{2}}{4} - \frac{\pi}{2} Z - \frac{\pi\sqrt{2}}{4} Z^2 \left(\frac{m}{M} \right)^{\frac{1}{2}} \right) \epsilon^4 + \dots \right] + \zeta^{\frac{3}{2}} \left[\frac{\sqrt{\pi}}{2} (Z+1)^{\frac{1}{2}} \epsilon^3 + \dots \right] + o\left(\zeta^{\frac{3}{2}}\right) \right\}, \quad (5.1)$$

where $\epsilon = [2\pi me^4/(h^2kT)]^{1/4}$. We have compared this result with those of DeWitt et al. [6] and find agreement in this limit, except for the $\zeta^{\frac{3}{2}}$ term where their result appears to be too large by a factor of 2. Note that their result is is only for an electron gas, so the ion-ion terms (which are dominant in the coefficients of ϵ^3 and ϵ^4 for large ζ) do not appear in their results.

One of the conclusions which can be drawn from (5.1) is the low density limit of the ionization profile, at least for high temperatures. Since the degree of ionization is roughly the electron pressure over the ideal non-interacting electron pressure, we deduce,

$$\lim_{r_b \to \infty} \frac{1 - \frac{Z_i}{Z}}{\left[(Z+1) \frac{a_0}{r_b} \right]^{\frac{3}{2}}} = \sqrt{\frac{2}{3} Z} \left(\frac{13.6052}{T_{\text{ev}}} \right)^{\frac{3}{2}}, \tag{5.2}$$

where a_0 is the Bohr radius. By contrast, the Saha formula [7]

$$\frac{Z_i}{Z} = \frac{1}{1 + A\zeta \exp(\gamma/T)} \tag{5.3}$$

gives

$$1 - \frac{Z_i}{Z} \propto \frac{\rho}{T^{\frac{3}{2}}}, \quad \text{instead of} \quad \propto \frac{\rho^{\frac{1}{2}}}{T^{\frac{3}{2}}},$$
 (5.4)

given by (5.2). Here ρ is the electron density. The difference in the power of ρ is presumably a combination of quantum and Coulomb effects.

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